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PREFACE

Atmospheric turbidity and visibility restrictions are perhaps the most obvious manifestations of air pollution. Historically, from the days of the caveman's primitive fire through the Industrial Revolution and onto the modern technological era, it has been clearly apparent that the emission of smoke, dust and fumes into the air decreases its clarity, and destroys scenic vistas. Until recently, however, there has not existed an adequate scientific understanding of the relationship between airborne particulate matter and reduced visibility, or the mechanisms by which aerosols interact with light rays to produce atmospheric turbidity.

This lack of knowledge has been a severe impediment to early efforts by air pollution control authorities to accurately quantify the extent of visibility reduction caused by particulate pollutants. The latter was evidenced by the initial attempts to set visibility standards in California, based simply on concentration of total suspended matter.

In the early 1960's, W. Stoeber and I at the California Institute of Technology concluded that such problems of visibility were amenable to scientific investigation and solution. Accordingly, we proposed to undertake a comprehensive study of the influence of aerosol characteristics on visibility. The Public Health Service, recognizing the potential value of such research, awarded the investigators a 3-year grant.

After the first year, the research project was transferred to the University of Washington, Seattle, where I, joined in time by Nasaki, Pueschel and Charlson, continued the work. Ultimately Charlson and his associates, Ahlquist and Waggoner, successfully expanded and deepened the scope of the research.

The history of this research attests to the principle that a sound scientific idea emerging at the proper time, adequately encouraged and supported,

can not only add to the fund of knowledge, but also contribute greatly to the technical solution of important social problems.

August T. Rossano
February 12, 1971

ABSTRACT

This report summarizes progress in measuring the optical properties of aerosols and in relating aerosol characteristics to visibility reduction made in the author's laboratory during the period 1965-1971. An instrument, the integrating nephelometer, which measures the scattering component of extinction, b_{sp}, was developed and used in several field studies. Measured b_{sp} and observer visibility have been shown to be highly correlated and to follow the Koschmieder relation. Measured b_{sp} is highly correlated (0.95 in Los Angeles) with suspended particle volume in the 0.1 to 1.0 μm size range. A useful correlation (0.56 to 0.92 at various sites) has been found between b_{sp} and particle mass as collected on a filter. Techniques have been developed to measure b_{sp} as a function of relative humidity for ambient and model aerosols. Water, absorbed by hygroscopic aerosols, as H_2SO_4, and/or deliquescent aerosols, as $(NH_4)_2SO_4$, make a substantial contribution to visibility reduction. Techniques were also developed to measure the absorption component of extinction, b_{ab}; to measure the forward/backward scattering ratio; and to determine b_{sp} as a function of wavelength.

This report was submitted in fulfillment of Grant No. R800665 by the University of Washington under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1, 1971, to December 31, 1974, and work was completed as of December 31, 1974.

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ACKNOWLEDGMENTS

We wish to acknowledge Prof. A.T. Rossano, who had the foresight in 1963 to begin this project. We certainly thank personnel of USPHS/D HEW, NAPCA and EPA for having provided funds for this twelve-year effort. We also thank the NSF under Grant GA 27662 which, although administratively unrelated to this visibility project, provided useful resources and opportunities for the data we report. Indeed, it is not possible to draw a hard line between the science supported by these two agencies, even though there were separate goals and purposes. Finally, we want to thank Prof. K.T. Whitby and his colleagues, Dr. George Hidy, the California State Air Resources Board, Dr. Rudolf Husar, Dr. John Winchester, and other colleagues who shared data with us.

SECTION I

INTRODUCTION

Air pollution, or more specifically the suspended particulate matter or aerosol, has dramatic effects on the optical properties of air. Visibility is often degraded from tens or hundreds of kilometers down to a few kilometers. In highly polluted areas such as Los Angeles, visual ranges as small as one kilometer occur.

The results reported here are from research started in 1962 with USPHS grant AP136. At that time, the consensus of experts was that the problem of visibility was too complex for generalization:

> "It seems apparent...that any relation which is found between visibility and particulate concentration...would be limited to the specific location and time period when the sampling was done. Like most atmospheric phenomena, these are very complex measurements in spite of their apparent simplicity."
>
> E. Robinson in Stern's 1962 edition of Air Pollution.

As reported in our publications and by others, the instrumental approach we developed has made visibility degradation one of the best understood and most easily quantified effects of air pollution.

A new instrument, the integrating nephelometer, was developed for our visibility investigations. This instrument has provided an objective measure of the optical effect of urban aerosol, and the measured scattering coefficient has been shown to be highly correlated with both visual range and mass concentration of particles, particularly those between 0.1 and 1.0 μm in diameter. A 1973 report of the State of California Air Resources Board recommends the integrating nephelometer as an instrument for routine air quality monitoring (Samuels, et al., 1973).

The following sections summarize current knowledge of aerosol properties necessary to describe integral effects of the aerosol-atmosphere system as they relate to the problem of visibility. Included is research by others as

well as that supported at the University of Washington. A list of publications supported by this grant is given in Appendix A.

SECTION 2

ATMOSPHERIC OPTICS AND VISIBILITY

It is convenient to define several parameters commonly used to describe atmospheric optics.

The extinction coefficient b_{ext} of a real atmosphere defines the change in intensity of light traversing a pathlength Δx by the Beer-Lambert law:

$$-\frac{\Delta I}{I} = -b_{ext}\,\Delta x$$

b_{ext} is the sum of two terms:

$$b_{ext} = b_{ext}\ (\text{gases}) + b_{ext}\ (\text{Particles})$$

$$b_{ext}\ (\text{gases}) = b_{Rg} + b_{ag}$$

where $b_{Rg}\Delta x$ is the fraction of incident light scattered into all directions by gas molecules in Δx.

$b_{ag}\Delta x$ is the fraction of incident light absorbed by gas molecules in Δx.

Our interest is in b_{ext} (particles), which can be broken down as follows:

$$b_{ext}\ (\text{particles}) = b_{ap} + b_{sp}$$

where $b_{ap}\Delta x$ is the fraction of incident light absorbed by particles in Δx.
$b_{sp}\Delta x$ is the fraction of incident light scattered into all directions by particles in Δx.

The observer visibility, or visual range, is that distance at which a black object can be just discerned against the horizon. Koschmieder (1924) showed that a turbid media, such as urban air, reduces the contrast (ratio of brightness of an object to the horizon brightness, minus one) of distant

objects as given by

$$C = C_0 \, e^{-b_{ext} s} \quad \text{(Middleton, 1968)},$$

where C_0 and C are the contrast relative to the horizon of an object at zero distance and at distance s. A black object has a C_0 of -1. Experiments have determined that typical observers can detect objects on the horizon with a visual contrast of 0.02 to 0.05. Assuming horizontal homogeneity of aerosol properties and illumination and a 0.02 detectable contrast, the visible range is

$$L_V = \frac{3.9}{b_{ext}}$$

For a contrast of 0.05,

$$L_V = \frac{3.0}{b_{ext}}$$

Usually the assumption is made that $b_{ext} = b_{sp}$.

b_{sp} can be calculated from known or assumed aerosol particle size distribution, concentration and refractive index, as discussed in Section 3.

SECTION 3

PARTICLE OPTICS

The atmospheric aerosol is composed of particles that range in size from smaller than 0.01 μm to larger than 10 μm diameter. The particles are of various chemical compositions and each particle can be a mixture of substances or a single substance. The integral optical effect of the aerosol particles is dependent on all of these parameters.

The integral properties of an aerosol can be expressed in a number of ways: b_{sp}, b_{ap}, condensation nuclei count, mass of particles per volume of air, etc. Conversion from one integral aerosol property to another is generally impossible without knowledge of the particle size distribution. Earlier work by this laboratory (Charlson, 1969; Charlson, et al., a,b 1974) has shown that aerosol optical parameters depend predominantly on (1) size distribution, (2) molecular composition, and (3) relative humidity.

PARTICLE SIZE

The optical properties of an individual particle depend on its effective area, its refractive index, and, to an extent poorly understood, its shape.

Aerosol particle size distribution may be graphed in a number of ways: (1) log (dN/dlnD) vs lnD, (2) dN/dlnD vs lnD, (3) dS/dlnD vs lnD, and (4) dV/dlnD vs lnD, as shown in Figures 1 and 2 for urban Los Angeles data taken during a period in 1969 by K.T. Whitby (1973).

When plotted in this way, the volume distribution is usually bi-modal with one maximum between 0.2 and 1.0 μm and a second maximum between 3 and 20 μm in diameter, as shown in Figure 3. Using Mie solutions for spherical particles, the optical scattering extinction coefficient (b_{sp}) per log size interval can be calculated and is shown in Figure 3 using the measured Pomona aerosol size distribution. A similar plot of volume distribution and b_{sp} from Garland (1973) is shown in Figure 4 for high relative humidity

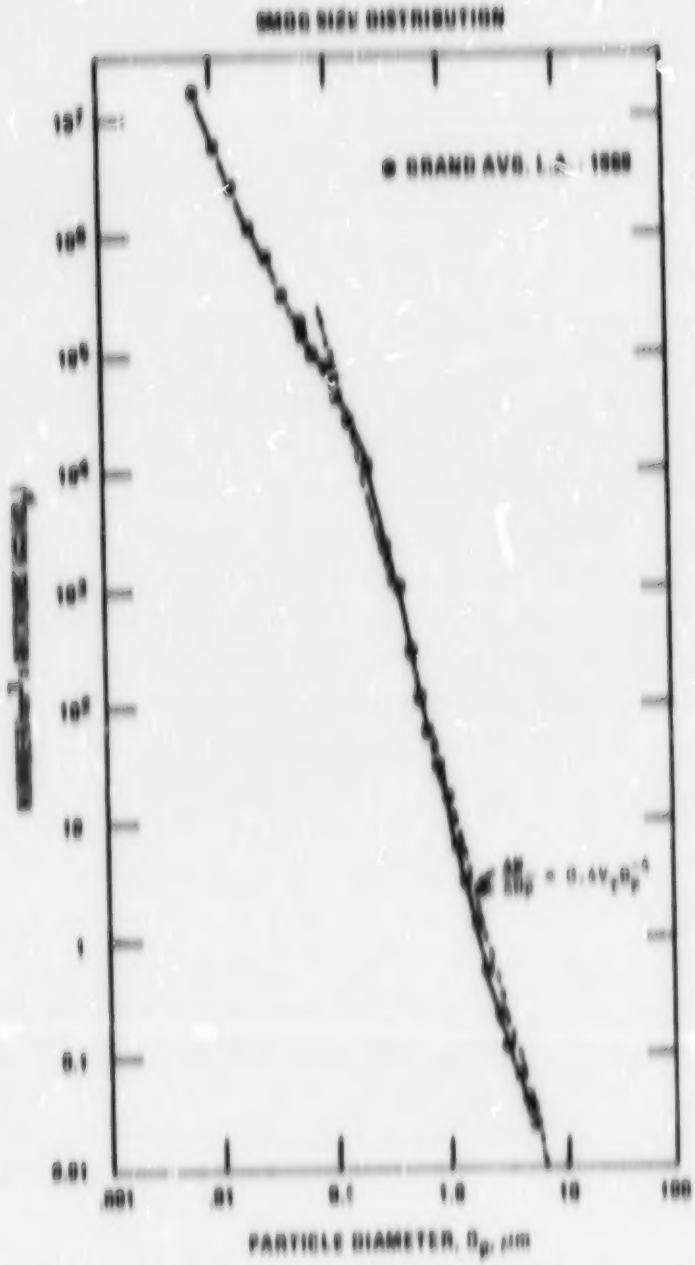
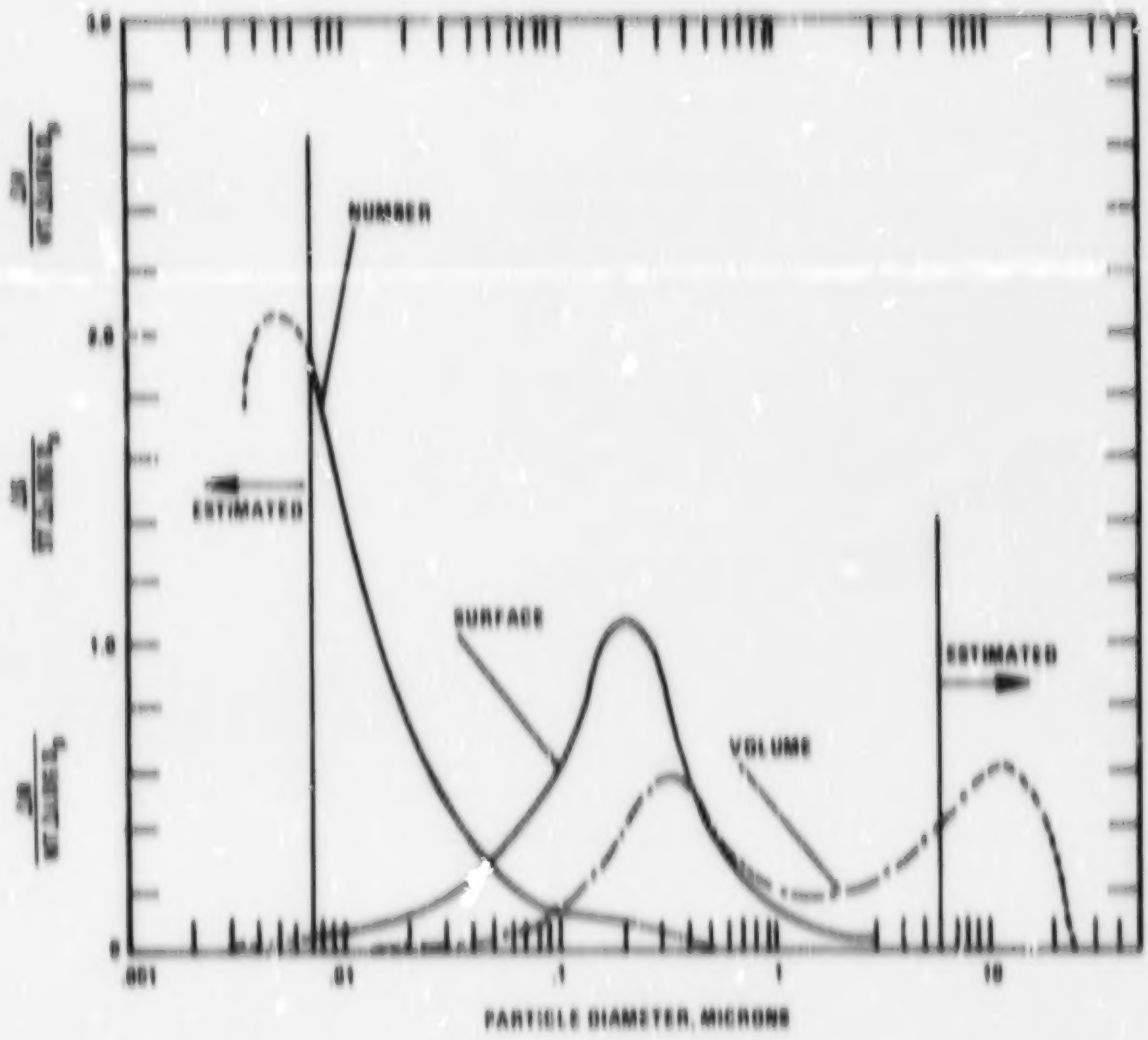


Figure 1. Figure 1 and 2 show different ways of plotting the same particle size distribution data taken during 1969 in Los Angeles. The size distribution was measured using a combination of electrostatic mobility and single particle optical counter techniques (Whitby, et al., 1972). Particle optical properties depend on particle surface or volume. Hence this figure shows that the optical properties of this sample are dominated by particles in the range 0.1 μm ≤ D ≤ 1 μm.


NUMBER
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SURFACE
VOLUME
ESTIMATED
.001
.01
.1
1
10
PARTICLE DIAMETER, MICRONS

Figure 2

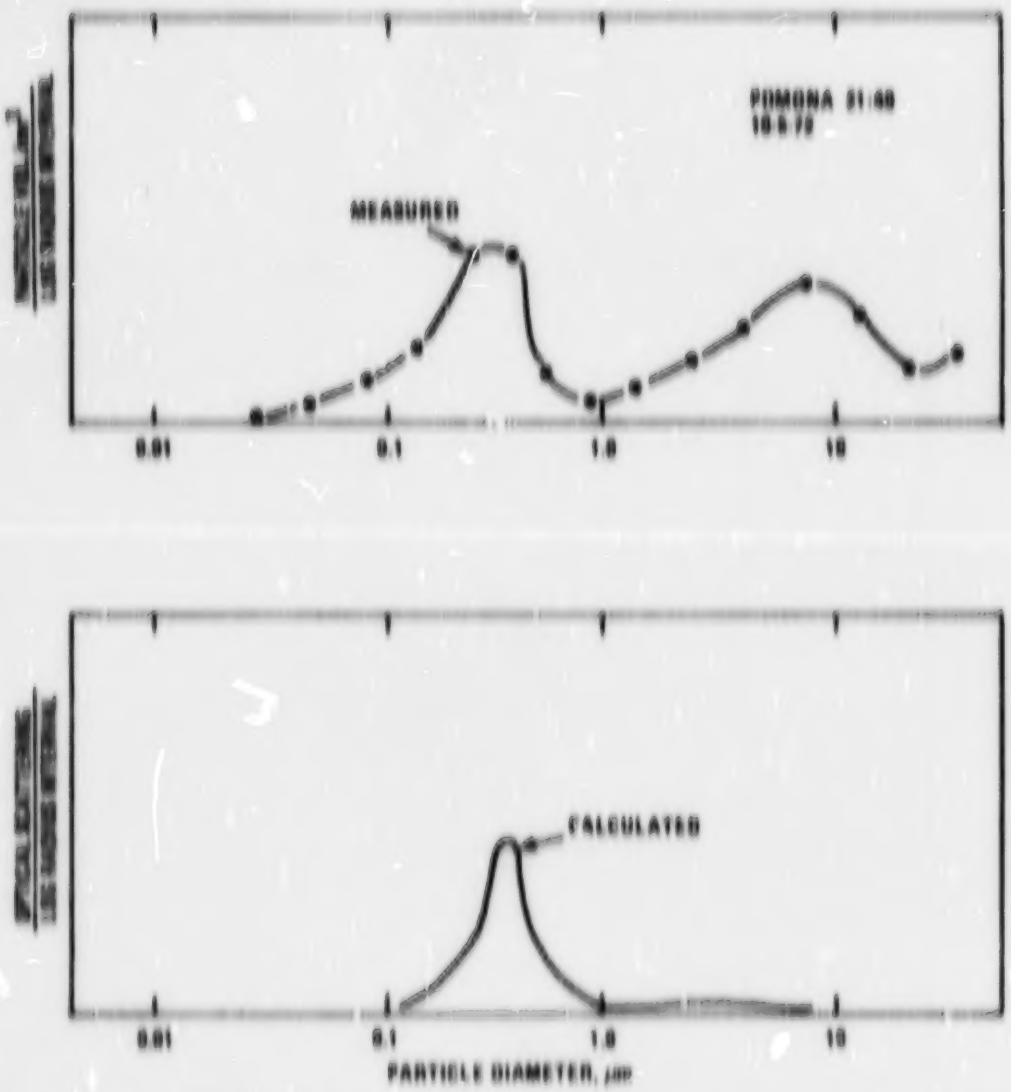

Figure 3. Top: Aerosol particle size distribution measured at Pomona during 1972 State of California Air Resources Board ACHEX program (Hidy, et al., 1975).

Bottom: Calculated optical scattering by particles, b_{sp}, for the measured size distribution. The particles are assumed to be spheres of refractive index 1.5.

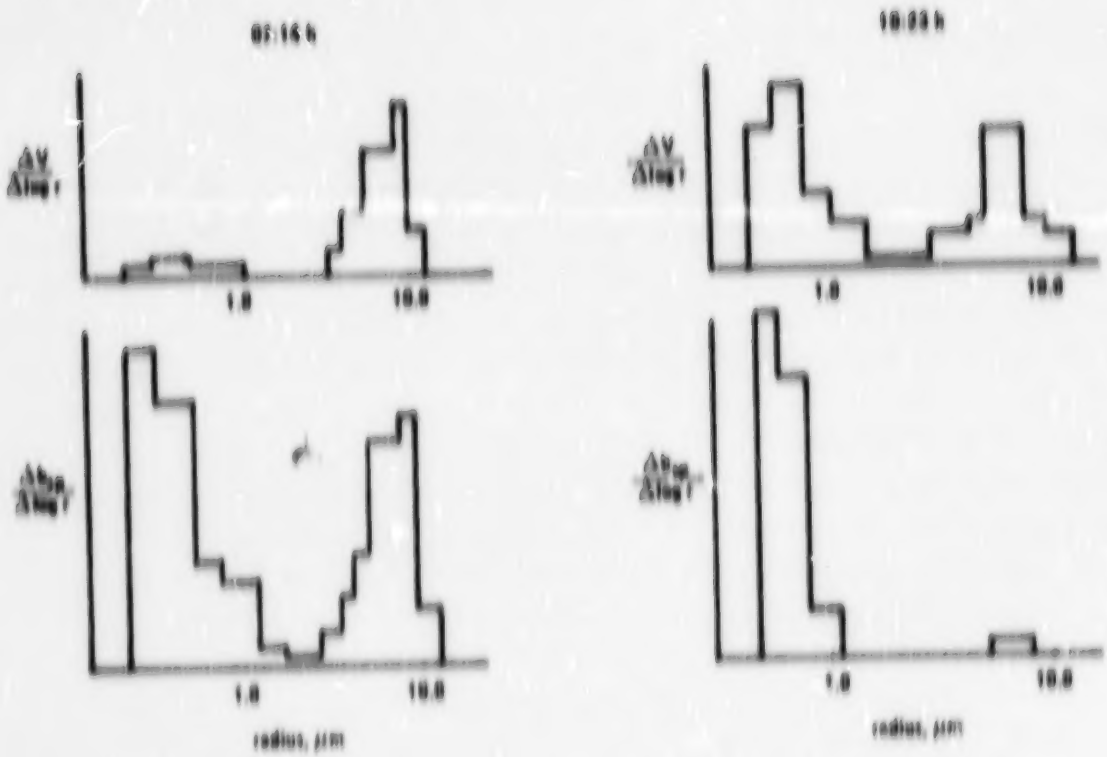

Figure 4. Light scattering coefficients in fog calculated from measured volume distributions of Garland et al. (1973), showing the dominant contributions of submicrometer particles to b_{sp}.

polluted British fog. It seems unusual that sub-micrometer aerosol particles dominate the aerosol scattering extinction in the visible spectrum although there clearly are cases in fogs, rain, snow, clouds and dust storms in which large particles influence or dominate visible extinction. A striking example of the relationship of measured particle scattering to measured particle volume in the 0.1 to 1.0 μm decade of particle size is shown in Figure 5.

The correlation coefficient of b_{sp}, measured with a nephelometer, and 0.1 to 1.0 μm particle volume, measured using electrostatic mobility and single particle optical counting techniques, was 0.95 at various locations in the Los Angeles basin. The correlation of b_{sp} with aerosol mass as collected on a filter is generally poorer, although still useful, as shown in Table 1.

MOLECULAR COMPOSITION

The particle interaction with water, biological effects and complex refractive index depend on the molecular composition. Therefore, it is important that the composition of various aerosol systems be classified, particularly insofar as this determines the imaginary part of the refractive index and hygroscopicity. Unfortunately, this is an area in which very little work has been done so far. Rasmussen and Went (1965) suggested that organic materials (terpenes) are a major source of atmospheric particles, but did not quantify their work adequately for application to optics. Junge (1954) has shown that the reaction products of SO_2 with water and ammonia play an important part in urban and rural aerosols, although he did not attempt to relate quantitatively the composition with optical effects. We have preliminary data suggesting that continental aerosol optics is often dominated by H_2SO_4 and the products of its neutralization with NH_3 (Charlson et al., 1974a; Charlson et al., 1974b).

There are two features of particulate chemistry which simplify the situation considerably in some locations. First, relatively pure (i.e., mole fraction >50%) molecular species (e.g. $(NH_4)_2SO_4$, H_2SO_4 or seasalt) dominate optical scattering in some atmospheric aerosols and second, certain compounds are found almost exclusively in the submicrometer fraction (Patterson and Wagman, 1974, Daubay and Stevens, 1973), as shown in Table 2 and in Figure 6.

The molecular nature of individual particles is a function of the source and removal mechanisms for these particles. The most important observable

TABLE 1. SUMMARY OF REPRESENTATIVE LIGHT SCATTERING- MASS CONCENTRATION STUDIES BY LOCATION AND MASS SAMPLING METHOD

Key: r = linear correlation coefficient A, B = regression coefficients in equation

$b_{sp,\ 550\ nm}(10^{-4}\ m^{-1}) = A + 10^{-2}B$ (mass concentration, $\mu g\ m^{-3}$)

Location (Reference) \ Mass Sampling Method	2.5 cm dia. open face, glass fiber filter			2.5 cm dia. Nuclepore filter			High Volume Air Sample			Glass fiber filter behind Impactor-Nucleo Cyclone		
	r	A	B	r	A	B	r	A	B	r	A	B
Los Angeles (Ensmenger, 1973)	0.83	-0.57	2.4	—	—	—	0.53	-0.89	3.3	0.83	0.33	3.7
Oakland, CA (This study)	0.69	-0.40	1.3	—	—	—	0.86	-0.61	2.4	0.79	0.36	3.2
Sacramento, CA (This study)	0.95	0.0	2.2	—	—	—	0.93	-0.56	2.8	0.98	0.33	4.4
New York, NY (Charlson, 1969)	—	—	—	0.92	-0.33	3.0	—	—	—	—	—	—
San Jose, CA (This study)	—	—	—	0.56	1.5	1.7	—	—	—	—	—	—
Seattle, WA (This study)	0.83	-0.98	3.5	(*)	—	—	0.73	-0.26	3.6	—	—	—
Boston, MA (Stevens, 1978)	—	—	—	—	—	—	0.86	-0.35	2.8	—	—	—

(*) Both types of filters were used

TABLE 2. ATOMIC ANALYSIS OF THE SEPARATED SMALL AND LARGE PARTICLES COLLECTED ON THE FILTERS SHOWN IN FIGURE 6b.

Element	Filter S Below 2 μm ng/m³	Filter L 2 to 10 μm ng/m³
Si	403 ± 160	1254 ± 463
S	3081 ± 700	389 ± 200
Cl	84 ± 30	400 ± 100
K	150 ± 60	213 ± 80
Ca	103 ± 40	1560 ± 400
Ti	62	192
V	4 ± 2	<3
Mn	5 ± 2	6 ± 2
Fe	131	395
Zn	45	15
As	20 ± 10	<4
Br	114	30
Pb	460	110

NOTE: The concentration of soil materials; Si, Fe, Ca, Ti in the large particle size and the products of gas to particle conversion; S, and automobile emission; V, Br, Pb in the small size (Daubay and Stevens, 1973).

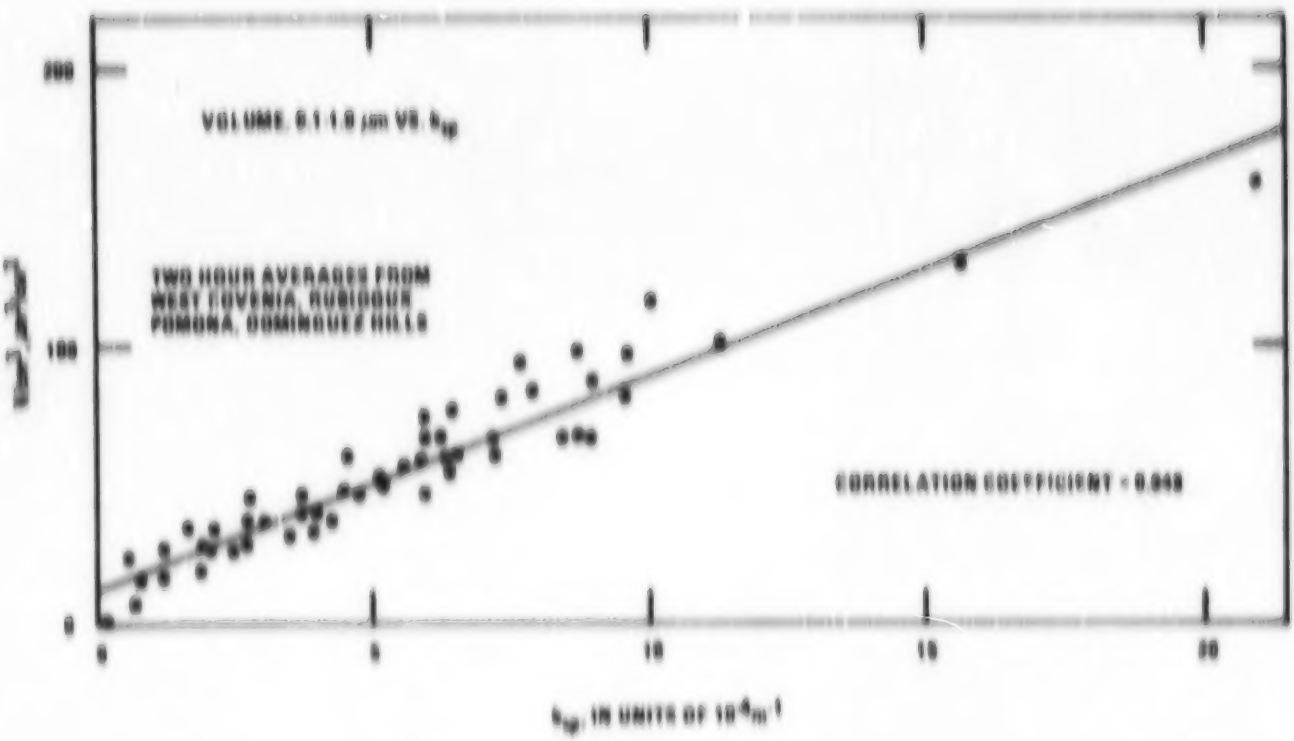

Figure 5. Plot of measured aerosol particle volume including only those of 0.1 to 1.0 μm in diameter versus measured b_{sp}. Measurements were part of State of California Air Resources Board ACHEX program (Hidy, et al., 1975)[7]. Data was supplied by Dr. Clark of North American Rockwell.

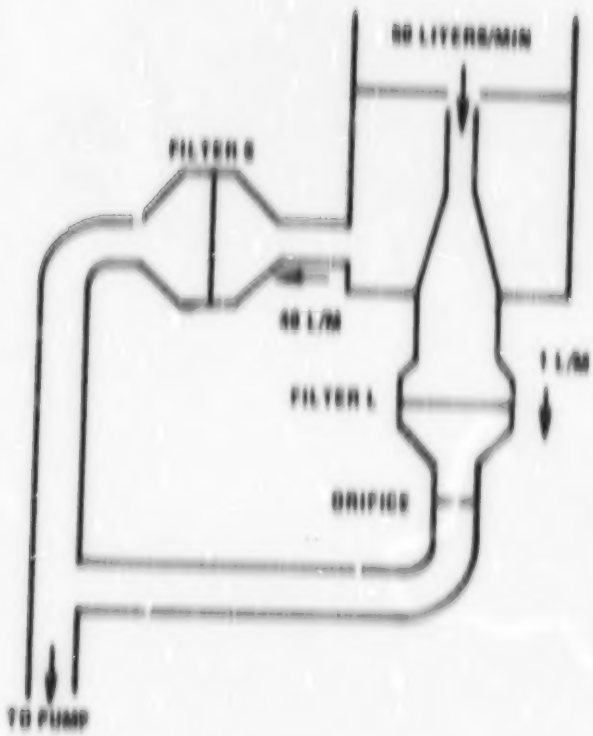

Figure 6a. Schematic view of a dichotomous sampler which contains a virtual impactor. The flow rate at the inlet is 50 liters per minute, and the flow rates at the outlets are 49 and 1 liters per minute (Loo and Jaklevic, 1974).

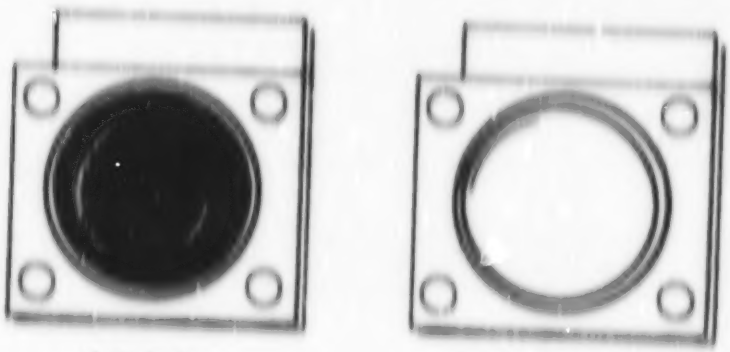

Figure 6b. Photograph of the two filters used in the dichotomous sampler for the 23 hour period beginning 10:15 30 August, 1973, at Wash. Univ. in St. Louis, Mo. The sampled air volume was 68 m^3. This reproduction shows, as does the original photograph, that most of the optical absorption is due to the small particle mode (Dzubay, 1973).

effect of composition on particle optics is the relationship of b_{sp} and relative humidity.

RELATIVE HUMIDITY

The humidity effects in aerosol optics fall into three categories:

RH ≤ 100%: particles between and above water clouds (including high RH haze);

RH > 100%: unactivated particles in water clouds and fog;

RH > 100%: activated cloud droplets.

Our efforts have been limited to the first two and are discussed in the following paragraphs.

RH < 100%

Since a large fraction of submicrometer particles are hygroscopic or deliquescent (Winkler, 1973; Junge, 1954; Hanel, 1971; Covert, 1974), the size distribution of an atmospheric aerosol, and hence its optical or climatological properties, depend largely on relative humidities, even at RH < 50%.

Figures 7, 8 and 9 show the total light scattering coefficient, b_{sp}, as a function of relative humidity for several different aerosol types as found in the real atmosphere. These curves are representative of those taken over a wide variety of locations and have certain highly reproducible features. First of all, it will be noted that light scattering always increases with humidity,, although for relatively hygrophobic systems the increase may be very slight up to extremely high RH (for example, Figure 9a). While for most aerosols, such as H_2SO_4 droplets, the curve increases monotonically, definite inflection points due to deliquescent salts (see Figures 7 and 9a) are seen frequently, indicating the dominance by rather pure inorganic substances such as $(NH_4)_2SO_4$.

The evolution of a distribution of droplets under conditions of changing, subsaturation RH modifies the optical interactions between radiation and particles, thus changing the temperature of the environment of the particles and hence in turn the relative humidity. This complex chain of events cannot be satisfactorily modelled until the parameters which go into the models (dependence of particle growth on chemistry, optical properties of saturated and supersaturated droplets, etc.) and the basic physical principles

Figure 7a. Averaged humidograms, Pt Reyes Lighthouse, California, 1630 24 Aug. 72 to 0600 26 Aug. 72.

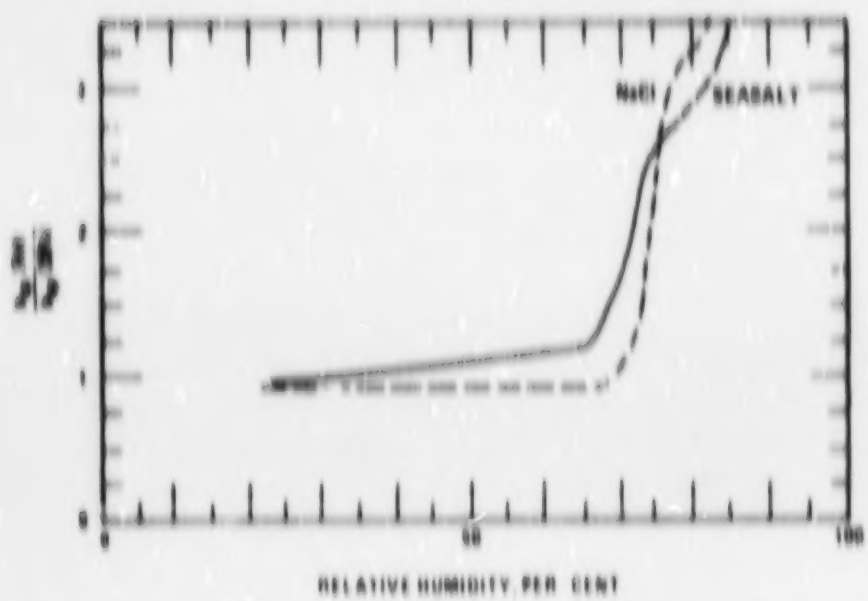

Figure 7b. Humidograms, laboratory aerosol, NaCl and Sea Salt.

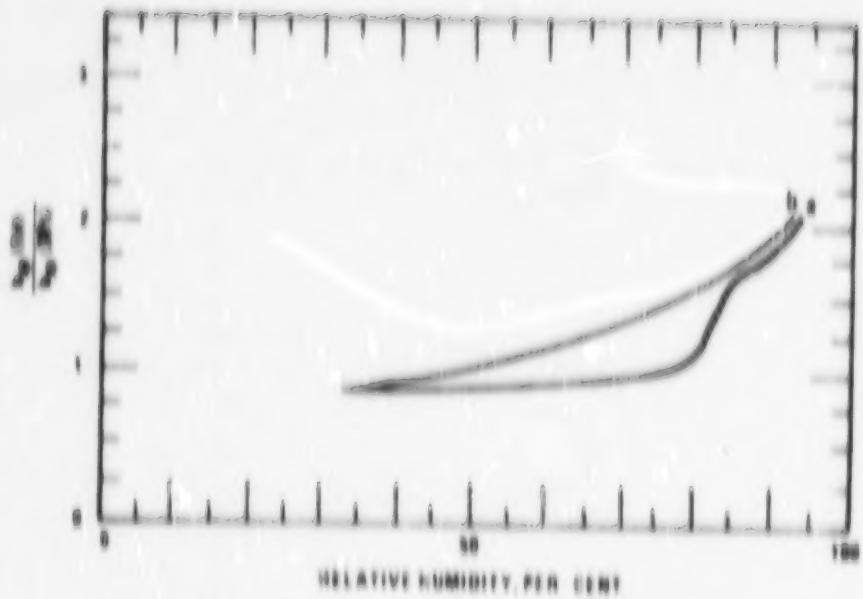

Figure 8a. Humidograms at Tyson, Missouri. a. 2130 24 Sep. 73, b. 1223 25 Sep. 73.

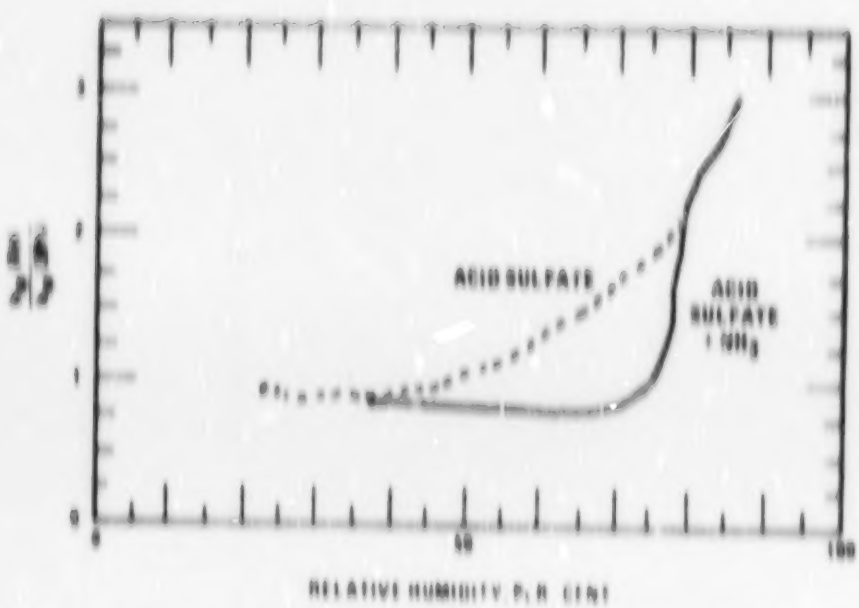

Figure 8b. Humidograms, lab acid sulfate aerosol with addition of 0.1 ppm NH_3.

Figure 9a. Averaged humidograms, Pasadena, California. a. 0212 to 1032 21 Sep. 72. b. 1300 to 1700 22 Sep. 72.

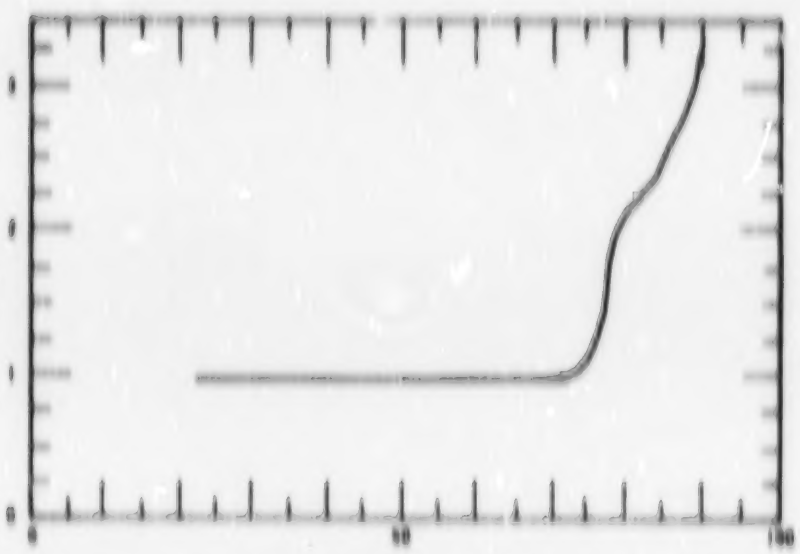

Figure 9b. Humidogram, $(NH_4)_2SO_4$ laboratory aerosol.

of the component processes are understood.

A system has been designed and operated by this laboratory that (over a period of about 120 seconds) sweeps the relative humidity of air containing aerosol particles from 30% to 95%. Changes in particle diameter are detected as changes in the scattering coefficient of the aerosol particles (Covert, 1974; Charlson et al., a,b 1974).

In the midcontinent region 30 km southwest of St. Louis, this system detected $H_2SO_4/(NH_4)HSO_4/(NH_4)_2SO_4$ as dominate materials in the 0.1 to 1 μm decade of aerosol size. Injection of sub ppm concentrations of NH_3 converted the $b_{sp}(RH)$ response characteristic of H_2SO_4 to that of $(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ is detected by comparing the value of relative humidity at the deliquescence point for the unknown sample with that of laboratory generated $(NH_4)_2SO_4$ aerosol. 98% of the time either H_2SO_4 or $(NH_4)_2SO_4$ was the dominant substance in terms of optical effect (Charlson et al., 1974a). Figure 10 shows non-urban turbidity and $SO_4^=$ and suggests a possible relationship between the two parameters similar to that found during our measurements near St. Louis.

RH > 100%, Unactivated Particles

When RH > 100%, and in the presence of suitable cloud condensation nuclei, some of the droplets grow to much larger sizes, forming fog and water clouds. The study of the processes leading up to the formation of the large drops is a cornerstone of cloud physics. In addition to the activated particles, there are unactivated particles which often outnumber the cloud or fog drops by orders of magnitude (Twomey, 1977), and which may still influence or even dominate some optical properties of clouds. Both light scattering and absorption by these unactivated particles may be important.

Figure 10a. Non urban turbidity, decadic extinction (Flowers et al., 1969).

Figure 10b. Non urban $SO_4^=$, $\mu gm/M^3$ (NASN data).

SECTION 4

TECHNIQUES FOR MEASUREMENT OF RELEVANT OPTICAL PROPERTIES

In the past several years our efforts have been focused on design and testing of methods to measure aerosol optical properties that directly determine aerosol radiative interactions. Methods for measurement of these relevant integral aerosol optical properties--namely, b_{ap}, b_{bap}, $b_{sp}(RH)$, and b_{sp}--are described in the following sections.

b_{sp}

Consider a layer of thickness ds illuminated by a parallel beam of wavelength λ and intensity $I_{o,\lambda}$. For perpendicular incidence, the intensity of light scattered into solid angle $d\Omega$ is

$$\frac{dI_\lambda}{d\Omega}(\theta)d\Omega = I_{o,\lambda}\beta_\lambda(\theta)ds.$$

A visibility meter using the operator's eye as a detector was devised by Beuttell and Brewer (1949) that geometrically performs the integration of $\beta_\lambda(\theta)$ over solid angle to measure $b_{sp,\lambda}$ (Middleton, 1968). Ahlquist and Charlson (1967) increased the original instrument sensitivity by using a photomultiplier tube to detect scattered light from a xenon flash lamp. Ahlquist et al. (1975, patent application) improved the sensitivity, stability and dynamic range by substituting an incandescent lamp for the xenon flash lamp and detecting the scattered light using digital photon counting techniques. This instrument, called an integrating nephelometer, is shown in Figure 11. Modern versions of Beuttell and Brewer's device have sufficient sensitivity to be calibratable in an absolute sense with b_{Rg}, the scattering coefficient of particle-free gases such as He, CO_2, CCl_2F_2.

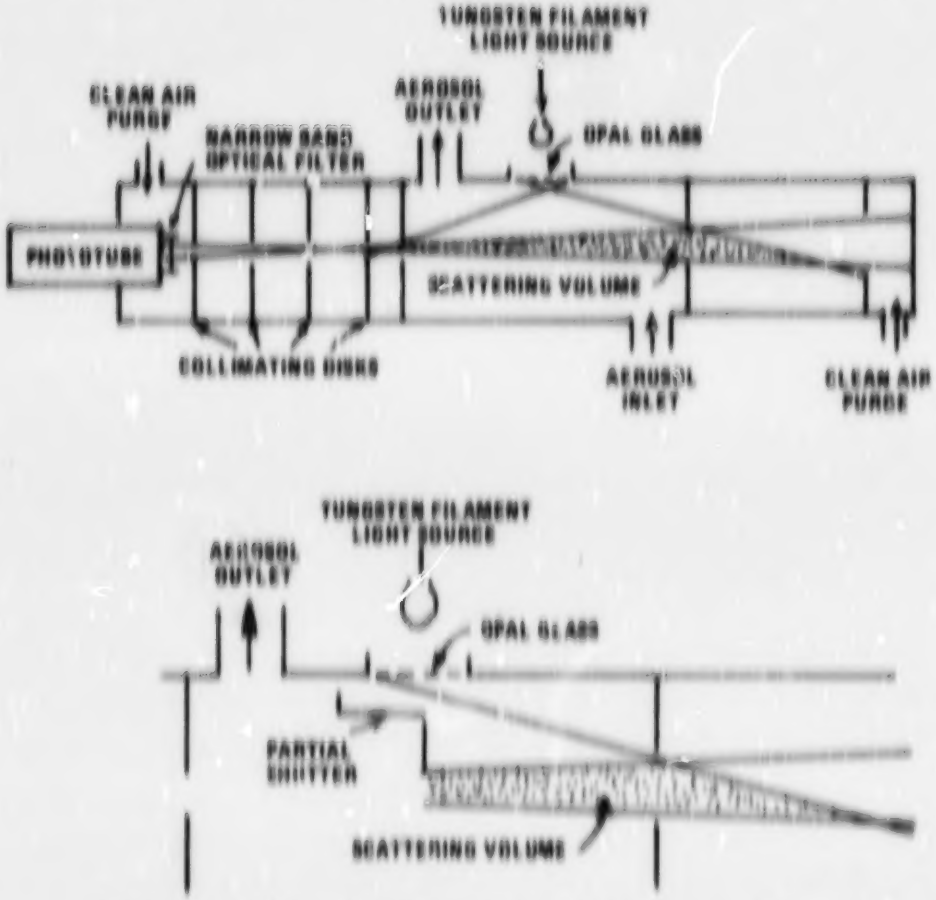

Figure 11. Diagram of nephelometer with enlarged view of the partial shutter. Without the shutter, the instrument integrates the particle scattering coefficient over ~7° to 170° to measure b_{sp}. With the shutter in place, the instrument integrates over ~90° to 170° to measure b_{bsp}.

The geometric errors of the instrument have been studied by Middleton (1968), Ensor and Waggoner (1970), Heintzenberg and Quenzel (1973), and Rabinoff and Herman (1973) and are estimated to be 10% or less for the aerosol particle size distributions normally found in the atmosphere.

The modern instrument is alternately filled with ambient and particle-free air and the difference in scattered light intensity is proportional to the scattering extinction coefficient due to aerosol particles, b_{ap}. The measured values of b_{ap} in the atmosphere range from $10^{-7}m^{-1}$ at Mauna Loa Observatory to $3 \times 10^{-3}m^{-1}$ in polluted Los Angeles (0.005 to 150 times the Rayleigh scattering coefficient at 530nm).

The integrating nephelometer has become an accepted instrument for measurement of aerosol scattering extinction. A series of patents, based on the designs of the authors of this report and covering various aspects of the nephelometer, have been issued to the University of Washington. Several hundred instruments have been produced and are in regular use for both research and monitoring. High sensitivity, multiwavelength instruments have been purchased by Institute für Meteorologie, Mainz, Germany, Air Force Cambridge Research Lab and the National Oceanographic and Atmospheric Administration.

The draft version of Volume I of the ACHEX[1] final report from Rockwell International to the Air Resources Board, State of California, recommends the integrating nephelometer for both long term monitoring and short term surveillance of aerosol properties.

b_{bsp}

An optically thin aerosol layer over a dark surface increases the albedo by scattering incident radiation backwards into space. The albedo per unit thickness of an aerosol layer illuminated by a zenith sun can be determined by integrating the aerosol volume scattering function over the backward hemisphere of scattering angle. A partial shutter, shown in Figure 11, can change the angle of integration of the nephelometer so that the scattered light intensity is proportional to the backward hemisphere scattering

[1] ACHEX Aerosol Characterization Experiment of the California Air Resources Board. Prime contractor is Rockwell International Science Center (Hidy et al., 1975).

extinction coefficient b_{bsp} due to aerosol particles. b_{bsp} normally is in the range 0.1 to 0.2 times the aerosol scattering extinction coefficient b_{sp}.

b_{sp}

The two aerosol parameters needed in simple radiative climatic models are the particle backward hemisphere scattering coefficient, b_{bsp}, and the particle absorption extinction coefficient, b_{ap}. There are a number of ways of measuring b_{ap}, and none is entirely satisfactory.

Long path extinction cannot be used because b_{ap} is $10^{-4}m^{-1}$ to $10^{-8}m^{-1}$ or smaller. Various techniques based on inverting angular scattering information have been used by Eiden (1966) and Grams et al. (1974), etc., but these methods require precise knowledge of the aerosol size distribution, and contain errors of unknown size and magnitude, since the scattering by irregular particles is calculated using Mie formulae for spheres. The absorption coefficient of collected aerosol samples can be estimated with low precision from measurement of the transmission of KBr pellets containing dispersed aerosol (Vala, 1973). Lindberg and Laude (1974) measured aerosol absorption by measuring the decrease of diffuse reflectance of a white powder when a small amount of aerosol is dispersed in it.

All of the above methods, in our opinion, are poorly suited for measurements in background locations. Measurement of the angular dependence of the aerosol volume scattering function is difficult when molecular scattering dominates. The methods of Vala and Lindberg require collecting an aerosol sample over several days, scraping the sample off the collecting surface, and dispersing the sample in another media. Any treatment of the sample that alters the aerosol size distribution will alter the optical absorption coefficient (Waggoner et al., 1973; Bergstrom, 1973). A different technique for measurement of b_{ap} has been developed in our laboratory that we believe is superior to those described above.

Atmospheric aerosol is collected by passing ambient air through a Nuclepore filter. The filter consists of a 10 μm thick film of polycarbonate plastic with 0.4 μm holes etched through it. The holes are etched along damage tracks from highly ionizing particles and are round and perpendicular to the surface of the film. Individual particles with a mean separation of

several diameters are collected on the surface of the filter. The filter and the particles are placed in an optical system that illuminates the particles and the filter with a parallel beam of, in this case, green light, and collects both direct transmitted and forward scattered light. The extinction or change in transmission between a clean filter and the filter plus aerosol is assumed to be the same as absorption by the same aerosol dispersed in a long column of air. Knowing the volume of air passed through the filter during collection of the aerosol, one can calculate the optical absorption coefficient due to particles, b_{ap}.

This method has been checked for accuracy using laboratory aerosols of known (including zero) absorption coefficient and is described by Lin et al. (1973). The disadvantages of the method center on errors introduced by sample alteration that may take place during collection, but the sample alteration is probably much less than in the techniques of Vois and Lindberg. The sample collection is simple and only requires 10 to 20 $\mu g/cm^2$ of aerosol on the filter. (Data is presented in Figure 12.)

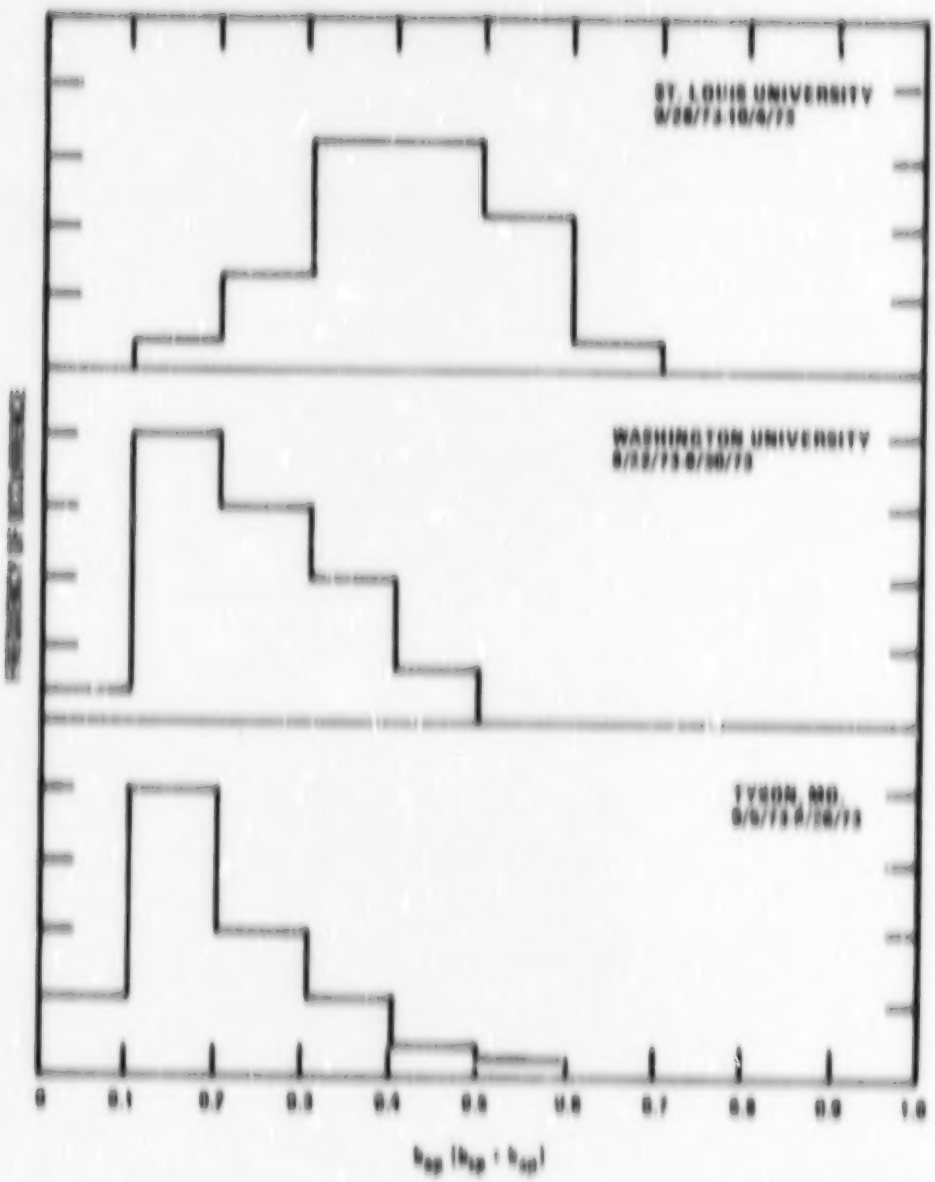

Figure 12. Histograms showing the absorption fraction of extinction at three sites in industrial-urban residential-urban and rural Missouri. b_{ap} (530 nm) was measured via the method of Lin (1973). b_{ap} (530 nm) was measured with a University of Washington nephelometer.

SECTION 5

ATMOSPHERIC MEASUREMENTS AND DATA

b_{sp} AND VISIBILITY

As discussed in Section 2, Koschmieder related b_{ext} to the distance at which a black object is just visible when viewed against the horizon sky. The distance of visibility is given by

$$V = \frac{3.9}{b_{ext}} \qquad \text{(Middleton, 1968)},$$

assuming aerosol homogeneity, uniform illumination and a 0.02 detectable contrast. Commonly it is assumed that $b_{ext} = b_{scat}$, i.e. $b_{abs} = 0$. Measurements of b_{scat} and observer visibility show good agreement with the formula above.

Horvath and Noll (1969) conducted a study in Seattle between total light scattering, b_{scat}, measured with an integrating nephelometer, and prevailing visibility observed by two separate people. Their results were in good agreement with the theoretical expression of Koschmieder for RH < 65% RH. Apparently the location of the nephelometer in a heated room caused a reduced RH in the light scattering measurements. In the cases where RH < 65%, the correlation between b_{scat} and the prevailing visibility was 0.89 and 0.91, respectively, with a coefficient in the Koschmieder expression of 3.5 ± 0.16 and 3.2 ± 0.25, respectively. This can be compared with the theoretical value of 3.9, indicating a slightly lower prevailing visibility than meteorological range. Since no ideal black targets were used (only trees, buildings, etc.), these would have caused just such a deviation.

Samuels et al. (1973) conducted the most extensive tests to date of the relationship of prevailing visibility to light scattering and various mass concentration measures as discussed earlier.

They conclude that b_{scat} as measured with the integrating nephelometer is a good predictor of prevailing visibility and that the regression analysis is in agreement with Koschmieder's theory. These workers noted that there was a smaller observed prevailing visibility than that predicted from theory and b_{scat} measurement, which they suggested was due to non-ideal black visibility targets.

MEASUREMENTS OF SCATTERING PARAMETERS

Under support from the Environmental Protection Agency, National Science Foundation and the California Air Resources Board, we have measured various aerosol scattering parameters in urban and rural locations in California, Colorado, Missouri and Washington. In all locations the incoming air was heated 5° to 20°C above ambient to lower relative humidity of the sample. The measured parameters were:

b_{sp} - Scattering extinction coefficient of particles at 530 nm. (Rayleigh at 530 nm = 0.15×10^{-4} m^{-1})

a - Wavelength dependence of b_{sp} parameterized

$$b_{sp} = K\lambda^{-a}$$

two values of a were computed from Red-Green b_{sp} and Blue-Green b_{sp}. Red is 640 nm. Blue is 430 nm. Green is 530 nm.

Scat. ratio - Ratio of half sphere back scatter to b_{sp} from particles at 530nm.

The sites were:

Richmond - Northeast corner of San Francisco Bay in vicinity of petrochemical plants.

Point Reyes - Coast Guard station on cliff 150 meters above the sea surface, 90 km NW of San Francisco.

Fresno - Central Valley of California, urban agricultural site.

Hunter Liggett - Rural California site 20 km inland from ocean. Local elevation 400 m. Local vegetation consisted of dry grass and sparse trees.

Cal. Tec. - Site on campus in Pasadena in Los Angeles basin.

Pomona - Site at county fairgrounds in inland area of Los Angeles basin.

Washington Univ. - Campus site located in residential area of St. Louis, MO.

Tyson - Rural area 25 km WSW of St. Louis.

St. Louis Univ. - Campus site in industrial St. Louis

Henderson - Site 10 km NE of Denver.

Trout Farm - Site 8 km N of Denver.

Table 3 lists the measured values at each site. For each measurement parameter, the range of that parameter containing 68% of the data is specified. For b_{ap}, the units are $10^{-4}M^{-1}$ and the range low to high contains 63% of data.

b_{ap} MEASUREMENTS

Using the technique described in Section 4 (Lin et al., 1973), we measured b_{ap} at three locations near St. Louis during fall of 1973. The sites are discussed in the previous section. The measurements are presented in Figure 12 as the ratio of b_{ap} to b_{ext}, where b_{ext} is the sum of b_{ap} and b_{sp}. The results are as expected in that the rural area has much less absorption than the industrial area. The magnitude of absorption is very high in the industrial location; b_{ap} is nearly equal to b_{sp}. In terms of reducing solar energy at the surface, at Tyson backscatter and absorption have equal effect. At St. Louis University absorption dominates.

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SECTION 6

CONCLUSIONS

In 1962, experts in the field considered the relationship of visibility to measureable aerosol parameters to be intractable (see the Robinson quotation on page i).

As described in Section 5, we now have a good understanding of the relationship of visibility to aerosol parameters, as well as instruments to measure these aerosol parameters. In the aerosol field the contributions of K.T. Whitby, B.Y.H. Liu and co-workers at the University of Minnesota cannot be over-emphasized.

We would summarize the result of the past 12 years of research on aerosol properties by ourselves and others as:

1. The integrating nephelometer is a useful instrument to measure the scattering component of extinction, b_{sp}.

2. Measured b_{sp} and observer visibility are highly correlated and follow the Koschmieder relation.

3. Measured b_{sp}, using a commercial integrating nephelometer, has been shown to have a very high correlation coefficient (e.g. 0.95 in measurements at several Los Angeles basin sites) with measured suspended particle volume concentration in the 0.1 to 1.0 um decade of particle diameter.

4. A useful correlation exists between b_{sp} and particle mass as collected on filters. Measured correlation coefficients at various sites range from 0.56 to 0.92.

5. As Whitby and others have shown, a plot of particle volume concentration per log radius interval usually has two log normal modes. Our optical results are consistent with this model.

6. Whitby's coarse particle mode, centered on 6 to 20 um diameter, is the product of mechanical operations, grinding fracture, etc., has the chemical properties of its local sources, usually has short atmospheric lifetime

and transport and usually has little or no optical effect, at least in all of our measurements.

7. The fine particle mode, centered on 0.3 to 0.6 μm diameter, is the product of high or low temperature condensation, coagulation and gas to particle conversion of natural or anthropogenic source materials. This mode is dominated by NH_4^+, $SO_4^=$, Pb, Br and organic matter, has long atmospheric lifetime and transport, and dominates light scattering.

8. Visibility reduction is predominately due to the fine particle mode.

9. Our measurements have shown that sulfates, sometimes as H_2SO_4/NH_4HSO_4 and sometimes as $(NH_4)_2SO_4$, dominate the small particle mode in rural Missouri.

10. In terms of aerosol optical scattering properties (i.e. b_{sp}, etc.), the differences between rural and urban sites seems to be small, with the exception of Los Angeles and clean coastal sites such as Point Reyes.

SECTION 7

EPILOGUE

As pointed out in the second paragraph of this report, when Prof. A.T. Rossano began this project, the probability of success seemed slim. The granting agencies (USPHS/DHEW) had to undertake support with an element of faith in the process of basic research. In retrospect, we feel this was warranted. The project successfully explained those aerosol characteristics which control visibility and developed an instrument, the integrating nephelometer, which is widely and successfully used. The entire project has been conducted as basic research as opposed to directed research.

In this day of increased control of research, of demands for relevance and application to natural needs, we are pleased to note that basic, undirected research still works. We feel it is safe for granting agencies to support some research with an element of faith that the results will be useful.

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